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(54) Direct use of ethylene oxide reactor gas to obtain ethylene carbonate and ethylene glycol

(57) A method wherein ethylene is oxidized in the vapour phase with molecular oxygen in the presence of catalyst to produce a gas composition comprising ethylene oxide, ethylene, carbon dioxide and water vapour and wherein at least a major portion of the ethylene oxide of a stream of the gas composition is converted in a reactor system to ethylene carbonate or a mixture of ethylene carbonate and ethylene glycol, which comprises introducing the stream of the gas composition in its substantial entirety to the reactor system.

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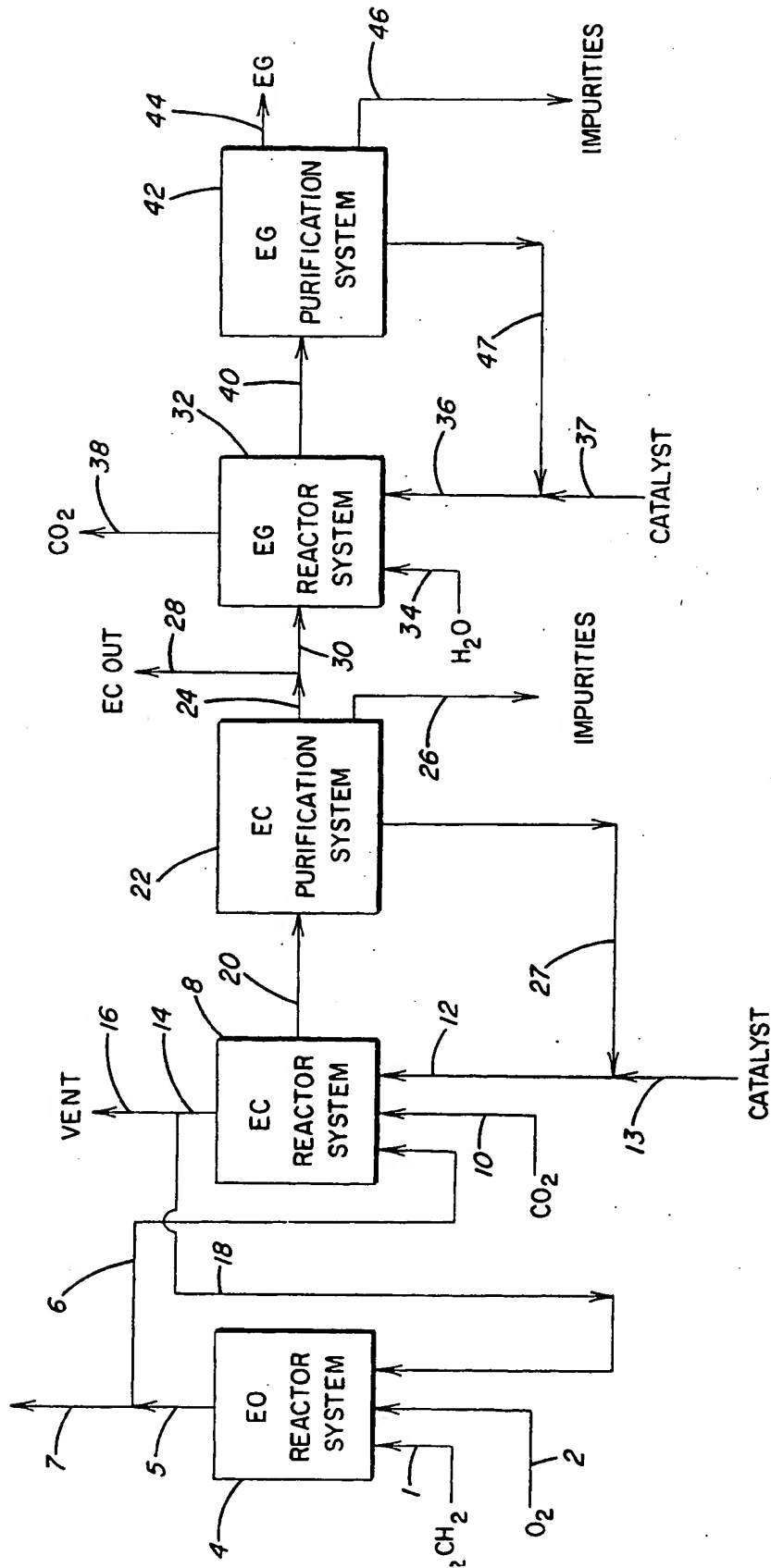


FIG. 1

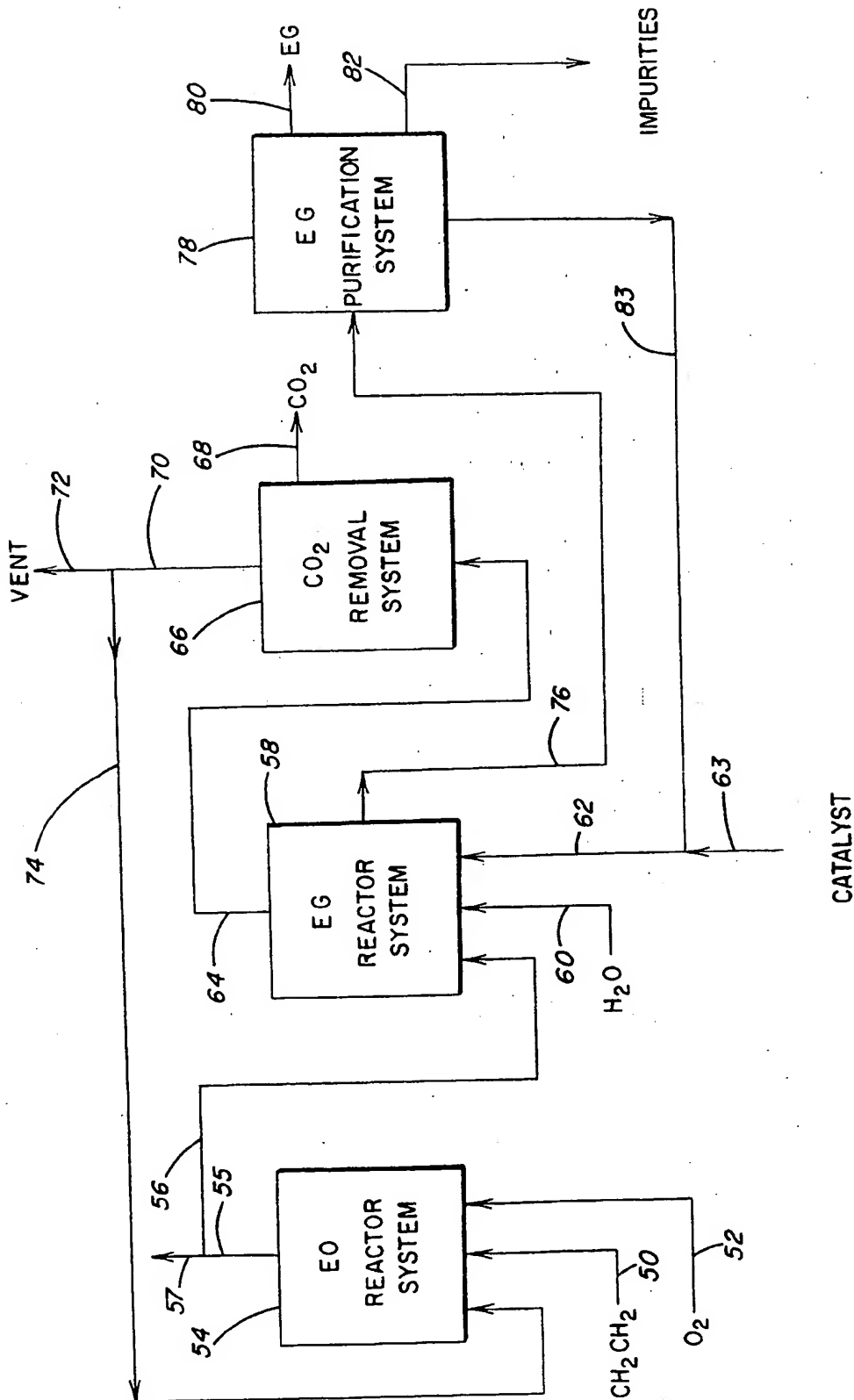


FIG. 2

SPECIFICATION

Direct use of ethylene oxide reactor gas

- 5 Processes for manufacturing ethylene oxide (EO) by the catalytic vapour phase oxidation of ethylene with molecular oxygen are well known and are described in Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd edition, volume 9, John Wiley & Sons, New York (1980), pages 439-459, 466-471. The compounds shown in Table 1, below, are generally present in gas compositions produced by such processes and their concentrations in these gas compositions typically fall within the ranges also shown. 5

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TABLE 1

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	Component	Concentration, mole percent	
15	EO	0.4 - 5	15
	CO ₂	0.2 - 15	
	C ₂ H ₄	2 - 98	
20	O ₂	0.2 - 7	20
	N ₂	Trace - 98	
25	Ar	Trace - 15	25
	H ₂ O	0.5 - 3	

- The above ranges are broad since ethylene oxide processes may employ, as the source of molecular oxygen, air, oxygen-enriched air, commercial oxygen (purity typically ≥ 95 mole percent O₂) which is generally obtained by the fractionation of liquid air, or pure oxygen, and since such processes may employ widely varying molar ratios of ethylene to oxygen. In many cases at least some of the nitrogen may be replaced with methane and/or ethane. Most often in commercial practice, ethylene oxide constitutes from about 1 to about 2 mole percent of the gas composition. 30

- 35 As may be ascertained from Table 1 and the above discussion, gas compositions produced by the catalytic vapour phase oxidation of ethylene with molecular oxygen are very dilute in ethylene oxide. In view of the presence of large amounts of other materials it has heretofore been regarded as necessary to remove ethylene oxide from the gas compositions prior to use in other processes. Indeed, United States Patent No. 4,233,221 states that ethylene is usually obtained from the direct oxidation of ethylene is usually not pure enough to be employed as a feed to an ethylene carbonate plant without prior purification. Ethylene oxide is removed from the gas composition generally by adsorption in a liquid such as water (Kirk-Othmer, supra), ethylene carbonate (U.S. Patent No. 4,221,727; U.S. Patent No. 4,233,221), or non-aqueous liquid (U.S. Patent No. 3,644,432). The ethylene oxide is then recovered by desorption and forwarded for use. 40

- Processes (1) for reacting ethylene oxide with carbon dioxide to produce ethylene carbonate, (2) for reacting ethylene oxide with water to produce ethylene glycol, and (3) for reacting ethylene carbonate with water to produce ethylene glycol, are well known. See, for example Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd edition, volume 11, John Wiley & Sons, New York (1980), pages 939-940, 955-956, and U.S. Patents No. 3,629,343; 4,117,250; 4,233,221 and 4,237,324. In each of these processes, however, either the source of the ethylene oxide or the ethylene carbonate, as the case may be, is undefined, or, if the ultimate source of ethylene oxide is identified as being produced by the catalytic vapour phase oxidation of ethylene, the ethylene oxide is removed from the gas composition leaving the ethylene oxide reactor prior to use. 45

- According to the present invention, in the method wherein ethylene is oxidized in the vapour phase with molecular oxygen in the presence of catalyst to produce a gas composition comprising ethylene oxide, ethylene, carbon dioxide and water vapour and wherein at least a major portion of the ethylene oxide of a stream of the gas composition is converted in a reactor system to ethylene carbonate or a mixture of ethylene carbonate and ethylene glycol, the improvement comprises introducing the stream of the gas composition in its substantial entirety to the reactor system. In short, the ethylene oxide need not be removed from the gas composition prior to conversion to ethylene carbonate or a mixture of ethylene carbonate and ethylene glycol. The equipment heretofore used for separation of ethylene oxide from the gas composition may accordingly be dispensed with and much of the energy expended in its operation saved. 50

- For a better understanding of the invention, reference may be made to the drawings in which:
Figure 1 shows diagrammatically one embodiment of the invention in which ethylene oxide produced by the catalytic vapour phase oxidation of ethylene is converted in a reactor system principally to ethylene carbonate which may optionally be hydrolyzed to ethylene glycol; and 55

- Figure 2 shows diagrammatically another embodiment of the invention in which ethylene oxide produced 60

by the catalytic vapour phase oxidation of ethylene is converted in a reactor system principally to ethylene glycol.

Referring now in more detail to Figure 1, ethylene is introduced through line 1 and molecular oxygen is introduced through line 2 to ethylene oxide (EO) reactor system 4. The molecular oxygen may be substantially pure or it may be in admixture with other gases. Typically, air, oxygen enriched air, or commercial oxygen is introduced through line 2. Ethylene oxide reactor system 4 is conventional and comprises one or more ethylene oxide reactors containing catalyst for catalyzing the vapour phase oxidation of ethylene to ethylene oxide. The catalyst is usually a silver-based catalyst although other types of catalyst may be used. When a plurality of reactors are used, they may be connected in series or in parallel or both in series and in parallel. The ethylene oxide-containing gas composition produced in ethylene oxide reactor system 4 leaves through line 5. If desired, a portion of this gas composition may be removed through line 7 for any of various uses. A stream of the ethylene oxide-containing gas composition produced in ethylene oxide reactor system 4, whether all or a portion of the total output of ethylene oxide reactor system 4, passes in its substantial entirety through line 6 to ethylene carbonate (EC) reactor system 8. Accordingly, the composition of the stream passing through line 6 is substantially the same as that of the gas composition produced in ethylene oxide reactor system 4. Ethylene carbonate reactor system 8 is likewise conventional and comprises one or more ethylene carbonate reactors in which ethylene oxide is reacted with carbon dioxide in the presence of a suitable catalyst to form ethylene carbonate. When a plurality of ethylene carbonate reactors are employed, they may be connected in series or in parallel or in both series and parallel. Further quantities of carbon dioxide over and above that contained in the gas composition passing through line 6 may be introduced as desired through line 10, although this is not necessary where the gas composition passing through line 6 contains sufficient carbon dioxide. Catalyst for catalyzing the ethylene carbonate-forming reaction is introduced through line 12. As needed, catalyst may be added through line 13.

The general conditions for the ethylene carbonate-forming reaction may vary widely. Superatmospheric pressures in the range of from about 5 to about 300 atmospheres and temperatures in the range of from about 85°C to about 250°C are usually employed. Often the superatmospheric pressure is in the range of from about 6 to about 150 atmospheres. From about 6 to about 50 atmospheres is preferred. Preferred temperatures are in the range of from about 100°C to about 200°C. The molar ratio of carbon dioxide to ethylene oxide introduced to the ethylene carbonate reactor system may also be widely varied. A molar ratio in the range of from about 0.9:1 to about 25:1 is generally used, although considerably greater ratios may be employed when desired. Often the molar ratio is in the range of from about 0.951:1 to about 20:1. It is preferred that the molar ratio of carbon dioxide to ethylene oxide be in the range of from about 1:1 to about 15:1.

The catalyst may be a single catalyst or it may be a combination of individual catalysts. Examples of useful catalysts are inorganic bases e.g. alkali metal hydroxide, alkali metal carbonate and alkali metal bicarbonate; halides (especially the chlorides, bromides and iodides) of the alkali metals (especially sodium and potassium); organic nitrogen bases e.g. tertiary amines, quaternary ammonium bases and salts of these nitrogen bases such as for example their carbonates and halides. For example, aliphatic tertiary amines e.g. trimethylamine; aromatic tertiary amines e.g. pyridine and quinoline; quaternary ammonium hydroxides e.g. tetraethylammonium hydroxide, benzyltrimethylammonium hydroxide, dialkyl pyridinium hydroxide and the carbonates, bicarbonates and halides of such substituted amines may be used to catalyze the reaction. Other catalysts are hydrazine and the hydrohalide salts thereof, guanidine and its salts and anion exchange resins containing quaternary ammonium halide groups. The preferred catalyst is either alkali metal halide or quaternary ammonium halide. The molar ratio of catalyst to ethylene oxide introduced to the ethylene carbonate reactor system is generally in the range of from about 0.005:1 to about 0.05:1. From about 0.001:1 to about 0.01:1 is preferred.

Gases from ethylene carbonate reactor system 8 are removed via line 14. Since these gases contain useful amounts of ethylene, they are for the most part recycled through line 18 to ethylene oxide reactor system 4. The gases, however, also contain inert materials which would tend to build up as the cycle continued. To maintain the concentration of inerts at an acceptable level, a portion of the gases passing through line 14 is vented through line 16.

Crude ethylene carbonate is passed from ethylene carbonate reactor system 8 to ethylene carbonate purification system 22 through line 20. In ethylene carbonate purification system 22 the crude ethylene carbonate is purified according to procedures known to the art to produce ethylene carbonate of desired purity which leaves through line 24 and impurities shown collectively leaving through line 26, although it is understood that various impurities may themselves be separated into separate streams in ethylene carbonate purification system 22, which streams may leave by a plurality of routes. Catalyst may be returned to ethylene carbonate reactor system 8 through line 27 and line 12 or it may be treated as an impurity and removed.

All or a portion of the purified ethylene carbonate leaving ethylene carbonate purification system 22 through line 24 may be removed through line 28 for any of various uses (e.g., as a solvent, as a stabilizer in lubricating oils, as a plasticizer, as a dispersing agent, as an extractant, as a blowing agent, as a reactant for producing other compounds, or for reconversion to ethylene oxide and carbon dioxide), or it may be passed via line 30 to ethylene glycol (EG) reactor system 32. When ethylene glycol is also produced in ethylene carbonate reactor system 8 it may be removed from the ethylene carbonate in ethylene carbonate

purification system 22 or it may be introduced along with the ethylene carbonate via line 30 to ethylene glycol reactor system 32. Ethylene glycol reactor system 32 is a conventional system and comprises one or more ethylene glycol reactors in which ethylene carbonate is hydrolyzed to form ethylene glycol and carbon dioxide. When a plurality of ethylene glycol reactors are employed in the system, they may be connected in series, or parallel, or in both of these. Water is introduced through line 34 and catalyst, when used, is introduced through line 36. As needed, catalyst may be added through line 37. Carbon dioxide and other gases, if any, are removed through line 38. All or a portion of the gas from line 38 may be returned to ethylene carbonate reactor system 8 through line 10, if this is desired.

The general conditions for the hydrolysis of ethylene carbonate may vary widely. Superatmospheric pressure in the range of from about 5 to about 150 atmospheres and temperatures in the range of from about 85°C to about 400°C are generally employed. Preferably the superatmospheric pressure is in the range of from about 20 to about 60 atmospheres. Preferred temperatures are in the range of from about 100°C to about 200°C. The molar ratio of water to ethylene carbonate introduced to the ethylene glycol reactor system may also vary widely. A molar ratio in the range of from about 0.9:1 to about 25:1 is usually employed. Typically the molar ratio is in the range of from about 0.95 to about 10. It is preferred that the molar ratio of water to ethylene carbonate be in the range of from about 1:1 to about 5:1.

Although no catalyst need be used, it is generally beneficial to employ catalyst. The catalyst may be a single catalyst or it may be a combination of individual catalysts. Examples of useful catalysts are alumina; acids e.g. sulfuric acid; and bases e.g. the carbonates, bicarbonates and hydroxides of alkali metals. When used, the molar ratio of catalyst to ethylene carbonate introduced to the ethylene glycol reactor system is generally in the range of from about 0.0005:1 to about 2:1. Typically, the molar ratio is in the range of from about 0.005:1 to about 1.5:1. From about 0.05:1 to about 1:1 is preferred.

Crude ethylene glycol is passed from ethylene glycol reactor system 32 to ethylene glycol purification system 42 via line 40. In ethylene glycol purification system 42 the crude ethylene glycol is purified according to procedures known to the art to produce ethylene glycol of desired purity which leaves through line 44. Impurities may be removed through line 46 or, if split into several streams, through a plurality of similar lines. Catalyst, when used, may be returned to ethylene glycol reactor system 32 through line 47 and line 36 or it may be treated as an impurity and removed.

Referring now to Figure 2, ethylene is introduced through line 50 and molecular oxygen is introduced through line 52 to ethylene oxide reactor system 54, which is conventional and corresponds to ethylene oxide reactor system 4 of Figure 1. The ethylene oxide and carbon dioxide-containing gas composition produced in ethylene oxide reactor system 54 leaves through line 55. If desired, a portion of this gas composition may be removed through line 57 for any of various uses. A stream of the ethylene oxide and carbon dioxide-containing gas composition produced in ethylene oxide reactor system 54, whether all or a portion of the total output of ethylene oxide reactor system 54, is passed in its substantial entirety through line 56 to ethylene glycol reactor system 58. Accordingly, the composition of the stream passing through line 56 is substantially the same as that of the gas composition produced in ethylene oxide reactor system 54. Ethylene glycol reactor system 58 is conventional and comprises one or more ethylene glycol reactors in which ethylene oxide is reacted with water in the presence of carbon dioxide to form ethylene glycol. Whether the ethylene oxide reacts with carbon dioxide to form ethylene carbonate as an intermediate which then reacts with water to form ethylene glycol and carbon dioxide, or whether the ethylene oxide is hydrolyzed directly to ethylene glycol has not been fully ascertained. See United States Patent No. 3,629,343. When a plurality of ethylene glycol reactors are employed in ethylene glycol reactor system 58, they may be connected in series or in parallel or in both of these. Water is introduced through line 60 and catalyst, when used, is introduced through line 62. As needed, catalyst may be added through line 63. Gases are removed through line 64 and introduced to carbon dioxide removal system 66, which is conventional. Separated carbon dioxide is removed through line 68 and the remaining gases are removed through line 70. Since the remaining gases contain useful amount of ethylene, they are for the most part recycled through line 74 to ethylene oxide reactor system 54. These gases, however, also contain inert materials which would tend to build up as the cycle continued. To maintain the concentration of inerts at an acceptable level, a portion of the gases passing through line 70 is vented through line 72.

The general conditions for operating ethylene glycol reactor system 58 may vary widely. Superatmospheric pressures in the range of from about 10 to about 180 atmospheres and temperatures in the range of from about 80°C to about 220°C are ordinarily employed. Often the superatmospheric pressure is in the range of from about 15 to about 60 atmospheres. From about 15 to about 40 atmospheres is preferred. Preferred temperatures are in the range of from about 90°C to about 150°C.

The molar ratio of water to ethylene oxide introduced to the ethylene glycol reactor system may also be widely varied. A molar ratio in the range of from about 0.9:1 to about 25:1 is ordinarily employed. Often the molar ratio is in the range of from about 0.95:1 to about 15:1. From about 1:1 to about 10:1 is preferred.

The molar ratio of carbon dioxide to ethylene oxide introduced to ethylene glycol reactor system 58 is susceptible to extremely wide variation. The molar ratio is usually in the range of from about 0.35 to about 25:1. Often the molar ratio of carbon dioxide to ethylene oxide introduced is in the range of from about 1:1 to about 20:1. From about 2:1 to about 15:1 is preferred.

Although no catalyst need be used in ethylene glycol reactor system 58, it is usually beneficial to employ catalyst. The catalyst may be a single catalyst or it may be a combination of individual catalysts. The

catalysts earlier discussed with respect to ethylene carbonate reactor system 8 and ethylene glycol reactor system 32 of Figure 1 are suitable for use in ethylene glycol reactor system 58 of Figure 2. When catalyst is used, the molar ratio of catalyst to ethylene oxide introduced to ethylene glycol reactor system 58 may be considerably varied, but it is usually in the range of from about 0.0001:1 to about 0.5:1. Often the molar ratio is in the range of from about 0.001:1 to about 0.3:1. From about 0.01:1 to about 0.2:1 is preferred.

Crude ethylene glycol is removed from ethylene glycol reactor system 58 and introduced to ethylene glycol purification system 78, which is conventional, via line 76. Ethylene glycol of the desired degree of purity is removed through line 80 while impurities are removed through line 82 or a plurality of such lines. Catalyst, when used, may be returned through line 83 and line 62 to ethylene glycol reactor system 58 or it may be removed.

Although systems 8, 22, 32, 42, 58 and 78 are shown as operating continuously, it will be evident that any or all of them may be operated batchwise when desired. Should it be desired not to purify crude product from any or all of reactor systems 8, 32, and 58, the corresponding purification systems 22, 42, and 78 may be omitted. Similarly, when it is desired not to separate carbon dioxide from the gas from ethylene glycol reactor systems 58, carbon dioxide removal system 66 may be omitted. Line 18 and/or line 74 may be omitted when it is desired not to recycle gases to ethylene oxide reactor systems 4 and 54, respectively.

It will be understood that various auxiliary equipment such as heat exchangers, valves, pumps, storage tanks and the like may be located as desired throughout the processes in keeping with good engineering practice.

In the illustrative example which follows, all parts are parts by weight and all percentages are percent by weight unless otherwise specified.

Example

A synthetic gas mixture simulating a gas composition produced by the catalytic vapour phase oxidation of ethylene with molecular oxygen, is prepared and contains 1.14 mole percent ethylene oxide, 17.0 mole percent carbon dioxide, 13.0 mole percent ethylene and 68.86 mole percent nitrogen.

The above synthetic gas mixture and an aqueous sodium iodide solution containing 20 weight percent sodium iodide are fed as separate streams to a mixing tee such that the molar ratio of water to ethylene oxide in the resulting feed composition is 5.7:1. The feed composition is introduced to a reactor which is a series of stainless steel tubing (outside diameter 0.25 inch; inside diameter 0.18 inch) coils having a total length of 75 feet, and which is maintained at 300 pounds per square inch gauge and 90°C to 95°C. The rate of introduction is such as to provide a three minute retention time within the reactor. The effluent from the reactor is passed into a Hoke cylinder containing ethanol cooled to 0°C. Gases not absorbed in the ethanol are passed through an automatic pressure controller to gas sample bombs and a wet test metre. A total of 0.35 mole of ethylene oxide is introduced to the reactor after which the reactor is shut down. Gas chromatographic analysis of the liquid in the Hoke cylinder shows it to have the composition shown in Table 2.

TABLE 3

Component	Concentration, weight percent
Water	20.2
Ethanol	67.4
Ethylene Glycol	9.5
First Unknown	0.8
Ethylene Carbonate	1.8
Second Unknown	0.3

The first unknown is identified by mass spectrometry as an alcohol, but the exact identity could not be determined. The second unknown is not seen by the mass spectrometer. No diethylene glycol is detected either by gas chromatography or mass spectroscopy.

The ethylene oxide conversion is 97.4 percent. Ethylene glycol selectivity is 88.4 percent and ethylene carbonate selectivity is 11.4 percent. The material balance on ethylene oxide fed and accounted for in product and unabsorbed gases is 101.5 percent.

Conventional hydrolysis, where in the ethylene oxide is absorbed by water from the ethylene oxide reactor gases and then desorbed, is not as selective toward ethylene glycol at low water to ethylene oxide molar ratios. For example, conventional hydrolysis at a water to ethylene oxide ratio of 4.2:1 gives an ethylene glycol selectivity of about 65.7 percent, a diethylene glycol selectivity of about 27 percent, and a triethylene glycol selectivity of about 2.3 percent.

Although the present invention has been described with reference to specific details of certain embodiments thereof, it is not intended that such details should be regarded as limitations upon the scope of the invention except insofar as they are included in the accompanying claims.

5 CLAIMS

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1. A method wherein ethylene is oxidized in the vapour phase with molecular oxygen in the presence of catalyst to produce a gas composition comprising ethylene oxide, ethylene, carbon dioxide and water vapour and wherein at least a major portion of the ethylene oxide of a stream of the gas composition is converted in a reactor system to ethylene carbonate or a mixture of ethylene carbonate and ethylene glycol, which comprises introducing the stream of the gas composition in its substantial entirety to the reactor system.
2. A method according to claim 1 wherein the catalyst is silver-based catalyst.
3. A method according to claim 1 or 2 wherein the gas composition contains less than about 5 molar percent ethylene oxide.
4. A method according to claim 1, 2 or 3 wherein the principal organic product of the conversion of the ethylene oxide in the reactor system is ethylene carbonate.
5. A method according to claim 4 wherein additional carbon dioxide is introduced to the reactor system.
6. A method according to claim 4 or 5 wherein the conversion is accomplished in the presence of catalyst.
7. A method according to claim 4, 5 or 6 wherein ethylene carbonate produced in the reactor system is subsequently converted by hydrolysis to ethylene glycol.
8. A method according to claim 7 wherein the ethylene carbonate is removed from the reactor system prior to the hydrolysis.
9. A method according to claim 8 wherein the hydrolysis is accomplished in the presence of catalyst.
10. A method according to claim 7 or 10 wherein the hydrolysis occurs in the reactor system.
11. A method according to claim 7 or 10 wherein the hydrolysis is conducted in the presence of excess water.
12. A method according to any of claims 4 to 11 wherein the conversion is accomplished at superatmospheric pressure in the range of from about 6 to about 50 atmospheres.
13. A method according to any of claims 4 to 12 wherein the conversion is accomplished at a temperature in the range of from about 100°C to about 200°C.
14. A method according to any of claims 4 to 13 wherein the molar ratio of carbon dioxide to ethylene oxide introduced to the reactor system is in the range of from about 1:1 to about 15:1.
15. A method according to claim 1, 2 or 3 wherein the principal organic product of the conversion of the ethylene oxide in the reactor system is ethylene glycol.
16. A method according to claim 15 wherein the conversion is conducted in the presence of excess water.
17. A method according to claim 15 or 16 wherein the conversion is accomplished in the presence of catalyst.
18. A method according to claim 15, 16 or 17 wherein the conversion is accomplished at superatmospheric pressure in the range of from about 15 to about 40 atmospheres.
19. A method according to any of claims 15 to 18 wherein the conversion is accomplished at a temperature in the range of from about 90°C to about 150°C.
20. A method according to any of claims 15 to 19 wherein the molar ratio of water to ethylene oxide introduced is in the range of from about 1:1 to about 10:1.
21. A method according to any of claims 15 to 20 wherein the molar ratio of carbon dioxide to ethylene oxide introduced is in the range of from about 1:1 to about 20:1.
22. A method according to any of claims 15 to 21 wherein the molar ratio of carbon dioxide to ethylene oxide introduced is in the range of from about 2:1 to about 15:1.
23. A method according to claim 1 and substantially as described with reference to and as illustrated in Figure 1 or 2 of the accompanying drawings.
24. A method according to claim 1 and substantially as described with reference to and as illustrated in the Example.